The Influence of Inhibitor Ions on Dissolution Kinetics of Al and Mg Using the Artificial Crevice Technique

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 Electrochemical and Solid-State Letters, 5 (2) B1-B4 (2002) [DOI: 10.1149/1.1429542]

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The effect of four anions on dissolution kinetics of Al and Mg in chloride-containing solution was investigated using the artificial crevice technique. Polarization curves for Al and Mg artificial crevice electrodes were obtained by first dissolving the artificial crevice electrode to a fixed depth at a high potential and then scanning the potential downward to the repassivation potential. Potential components were obtained by fitting the polarization curve to an equation describing activation overpotential and ohmic potential drops. Of chromate, dichromate, molybdate, and nitrate, only nitrate was found to inhibit the dissolution kinetics of Al artificial crevice electrodes. In contrast, all anions inhibited the dissolution kinetics of Mg artificial crevice electrodes. The results indicate that the mechanism of localized corrosion inhibition of Al alloys by chromate must be something other than inhibition of anodic dissolution in an active pit or crevice.

High strength Al alloys such as AA2024-T3 are widely used in aircraft applications, but are extremely susceptible to localized corrosion. In order to protect them from localized corrosion, protective coatings containing inhibitors, typically chromates, must be used. Chromates (or dichromates) dissolved in solution are also extremely effective in inhibiting corrosion, even at dilute concentrations.[1,2] However, the mechanism of corrosion inhibition by chromate remains unclear. One of possible explanations is anodic inhibition, in the sense that chromates might greatly reduce the local dissolution kinetics of Al alloys in pits or crevices. The repassivation potential is the lowest potential at which the critical current density for pit growth can be maintained.[3] Since pits or acidic crevices must maintain a minimum or critical current density in order to avoid repassivation, a decrease in the pit or crevice dissolution rate as a function of potential could inhibit localized corrosion by increasing the repassivation potential, which is the potential required to achieve the critical current density.[3]

Artificial pit or ‘‘lead in pencil’’ electrodes have been used by researchers previously to study pit growth kinetics.[4-11] The artificial pit electrode geometry forms a single pit in which the whole electrode area is active, generates a natural pit environment, and provides an ideal one-dimensional transport condition. The artificial crevice electrode is similar to the artificial pit electrode, except that a metal foil instead of a wire is used to create a recessed band instead of a recessed disk.[10,11] Hydrogen bubbles can escape easier from this geometry, so artificial electrodes are useful for studying the localized corrosion kinetics of Al or Mg, in which copious hydrogen is evolved.

Artificial crevice electrodes have been used to study the effect of dichromate on Al dissolution in chloride solutions.[11] Charge density was measured in potentiostatic experiments. The addition of dichromate ions did not suppress the active dissolution, suggesting that the mechanism of localized corrosion inhibition by dichromates is something other than anodic

inhibition of Al dissolution in the pit or crevice environment. In this study, the influence of dichromates, chromates, nitrates, and molydates on AA1100 and Mg dissolution kinetics was studied using a potentiodynamic approach. AA1100, which is 99% pure, was used as an analog of the matrix phase of typical Al alloys. Mg was studied because it is also strongly inhibited by chromates, and is relevant to the behavior of Mg-rich intermetallic particles in 2xxx Al alloys.

Experimental

AA1100 and 99.9% Mg foils of 50.8 and 125 μm thickness, respectively, were sandwiched between two transparency sheets using epoxy. The foils were 5 mm wide, and other details of the artificial crevice cell were described in the previous paper.[11]

Al and Mg artificial crevice electrodes were potentiostatically polarized at 0 and -0.5 V saturated calomel electrode (SCE), respectively, until reaching a depth-to-width ratio of 1.5 (the width of the crevice being determined by the foil thickness). The potential was then scanned down to the repassivation potential at a rate of 1 mV/s for the Al electrodes. The polarization curves of the Al crevice electrodes were determined in this fashion. For the Mg electrodes, following the potentiostatic polarization at -0.5 V SCE, the potential was stepped to -0.8 V SCE and then scanned downward to the repassivation potential at a rate of 1 mV/s. For both Al and Mg, the electrolytes studied were 0.5 M NaCl with and without the presence of 0.05 or 0.5 M dichromate, chromate, molybdate, or nitrate inhibitor ions. Conductivities of various solutions used in this work were measured with a YSI 3200 conductivity meter.

Results and Discussion

Figure 1 shows the effects of various inhibitor ions on the polarization curves of Al artificial crevice electrodes. These curves were measured by scanning downward from the highest potential. The potential at which the current drops rapidly is considered to be the repassivation potential. The curves in Fig. 1 show that nitrate was the only species that effectively inhibited the anodic dissolution kinetics of the Al crevice electrode relative to the pure NaCl solution. Since chromate and dichromate are well known as inhibitors for Al corrosion, these results indicate that the mechanism must be something other than anodic inhibition of active dissolution, supporting the finding of the previous paper.[11] Nitrate was found to have only a minor influence at a concentration of 0.05, but a much larger effect at 0.5 M. The influence of nitrate in solution might be related to an increase in the crevice pH associated with nitrate reduction.[12] The fact that nitrate has a significant inhibiting effect on the dissolution of an Al artificial crevice indicates that this technique is suitable for the determination of Al anodic inhibition.

During the downward scan, ohmic control is dominant, as is determined by a potential component analysis. The applied potential, E_{tot}, is composed of the following components[8]

$$E_{tot} = E_r + \eta s + \Delta V_\Omega \qquad [1]$$

where E_r is the thermodynamic reversible potential with respect to the SCE reference electrode (-1.903 V SCE for Al and -2.613 V SCE for Mg), ηs is the surface overpotential, and ΔV_Ω is the ohmic potential drop. Furthermore, Tafel kinetics can be assumed and the ohmic potential drop can be divided into portions inside the crevice, $\Delta V_{\Omega crev}$, and outside of the crevice, $\Delta V_{\Omega ext}$

$$\eta s = b \log[i/i_0] \qquad [2]$$

$$\Delta V_{\Omega} = \Delta V_{\Omega crev} + \Delta V_{\Omega ext} \quad [3]$$

where b is the Tafel slope, i is current density, and i_0 is exchange current density. The two ohmic potential drops can be further specified. The ohmic potential drop in the crevice is given by the crevice current, I, the crevice solution conductivity, σ_{crev}, the effective crevice depth, d_{eff}, which is an average of the depth during the downward scan, and the crevice area $A = w \times t$, where w and t are foil width and thickness, respectively

$$\Delta V_{\Omega crev} = (Id_{eff})/(A\sigma_{crev}) = (id_{eff})/\sigma_{crev} \quad [4]$$

As a result of the downward potential scan, the crevice depth increases by an amount Δd from the initial depth d_0 . The effective crevice depth during the growth, d_{eff}, was considered to be an average

$$d_{eff} = d_0 + 0.5\Delta d \quad [5]$$

The initial crevice depth and change in depth can be determined from the charge passed.[11] The ohmic potential drop outside of the crevice is calculated from the primary resistance of a band electrode of dimension $w \times t$ [13]

$$\Delta V_{\Omega ext} = IR_{ext} = I\left(\frac{1}{\Pi\sigma_B w}\right)\ln\left(\frac{4w}{t}\right) = i\left(\frac{t}{\pi\sigma_B}\right)\ln\left(\frac{4w}{t}\right) \quad [6]$$

where σ_B is conductivity of the bulk electrolyte. The conductivities of the various solutions studied are listed in Table I. Combining equations

$$E_{tot} = E_r - b\log(i_0) + b\log(i) + i\left[\frac{d_{eff}}{\sigma_{crev}} + \left(\frac{t}{\pi\sigma_B}\right)\ln\left(\frac{4w}{t}\right)\right] \quad [7]$$

The i-E data were fitted to Eq. 7 to determine the voltage components and extract values of the unknowns, b, i_0, σ_{crev} (assumed to be constant down the crevice), which are listed in Table II. The fits to the Al and Mg data were all quite good, with R^2 values greater than 0.97. Figure 2 shows the voltage components as a function of applied potential for pure Al in 0.5 M NaCl. The Tafel slope is higher for most solutions containing inhibitors relative to the chloride solution. However, the values for b and i_0 are interrelated and cannot be independently determined.[14] The product $-b\log(i_0)$ is large compared to $b\log(i)$ and dominates the surface overpotential term because of the magnitude of i_0, so it represents the shift in the curve associated with the surface overpotential. The product $-b\log(i_0)$ is higher for the cases with the added ions, in particular for 0.5 M NaCl + 0.5M nitrate, the case that exhibited a strong inhibition.

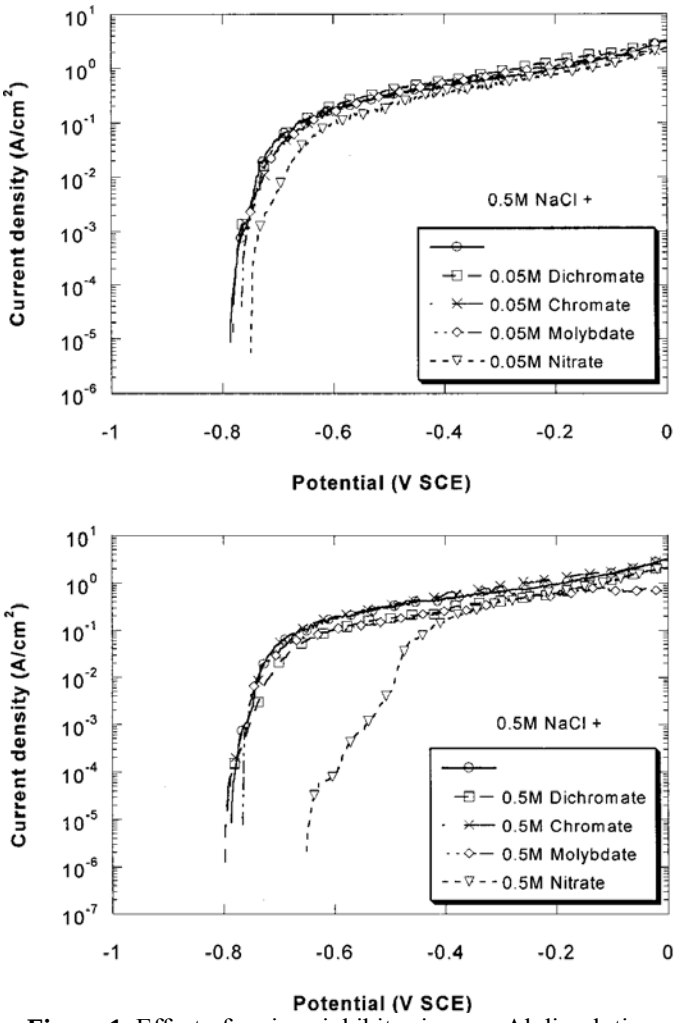

Figure 1. Effect of various inhibitor ions on Al dissolution kinetics in 0.5 M NaCl containing (a) 0.05 M inhibitor, (b) 0.5 M inhibitor.

Table I. Conductivity of various solutions.

Solution	σ_B (mS/cm)
0.5 M NaCl	44.0
0.5 M NaCl, 0.05 M dichromate	58.5
0.5 M NaCl, 0.05 M chromate	50.5
0.5 M NaCl, 0.05 M molybdate	48.4
0.5 M NaCl, 0.05 M nitrate	47.2
0.5 M NaCl, 0.5 M dichromate	100.8
0.5 M NaCl, 0.5 M chromate	103.8
0.5 M NaCl, 0.5 M molybdate	85.6
0.5 M NaCl, 0.5 M nitrate	76.5

Table II. Values determined from Al artificial crevice experiments.

Solution	E_{rp} (V SCE)	$\log(i_0)$ (A/cm^2)	b (V/dec)	$-b\log(i_0)$ (V/dec)	σ_{crev} (mS/cm)
0.5 M NaCl	—0.787	—34	0.037	1.258	16
0.5 M NaCl, 0.05 M dichromate	—0.785	—23	0.058	1.334	32
0.5 M NaCl, 0.05 M chromate	—0.782	—37	0.034	1.258	20
0.5 M NaCl, 0.05 M molybdate	—0.766	—18	0.074	1.332	33
0.5 M NaCl, 0.05 M nitrate	—0.750	—22	0.061	1.342	17
0.5 M NaCl, 0.5 M dichromate	—0.799	—29	0.045	1.305	9.0
0.5 M NaCl, 0.5 M chromate	—0.797	—21	0.064	1.344	36
0.5 M NaCl, 0.5 M molybdate	—0.767	—28	0.044	1.232	13
0.5 M NaCl, 0.5 M nitrate	—0.652	—26	0.061	1.586	32

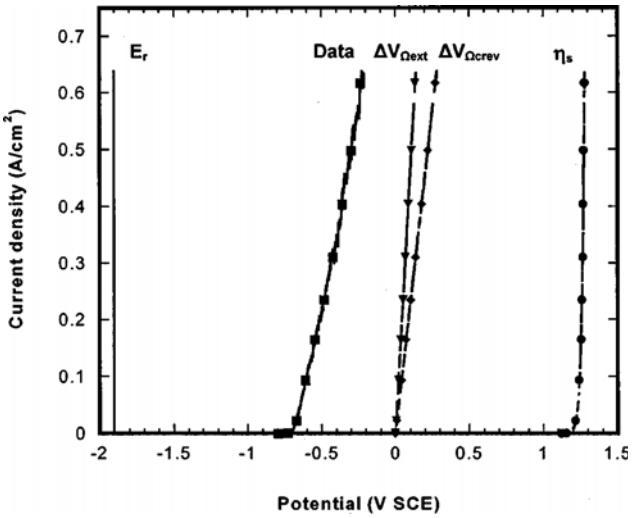

Figure 2. Voltage component calculation for pure Al in 0.5 M NaCl.

Since the total potential at each current density is the sum of the various components, it is possible to determine the controlling factors.[15] At high potentials, the current varies linearly with potential and the slope of the crevice polarization curve is controlled primarily by the ohmic potential drop in the crevice. However, the position of the crevice polarization curve on the potential axis is determined by the sum of the reversible potential and the surface overpotential term. The activation term is weakly dependent on current density (the dependence is logarithmic). Hence, at high potentials, the ohmic drop dominates the dependence of the potential on the current density. At low potentials, where the current is small, the iR drop becomes small and the activation term dominates.

Mg corrosion is also strongly inhibited by chromates. Furthermore, the effect of chromate on Mg is relevant to high strength Al alloys such as AA2024-T3, which contains a Mg-rich intermetallic phase, Al_2CuMg. The approach used on Al was applied to Mg artificial crevice electrodes in order to test whether it is capable of discerning the inhibition associated with chromates. Figure 3 shows the effect of the various inhibitor ions on the polarization curves of Mg crevice electrodes. All of the inhibitors were found to significantly reduce Mg anodic

dissolution kinetics relative to pure NaCl solution. This behavior is in contrast to that of Al artificial crevices, and proves that the technique can, in fact, detect the influence of an anodic inhibitor.

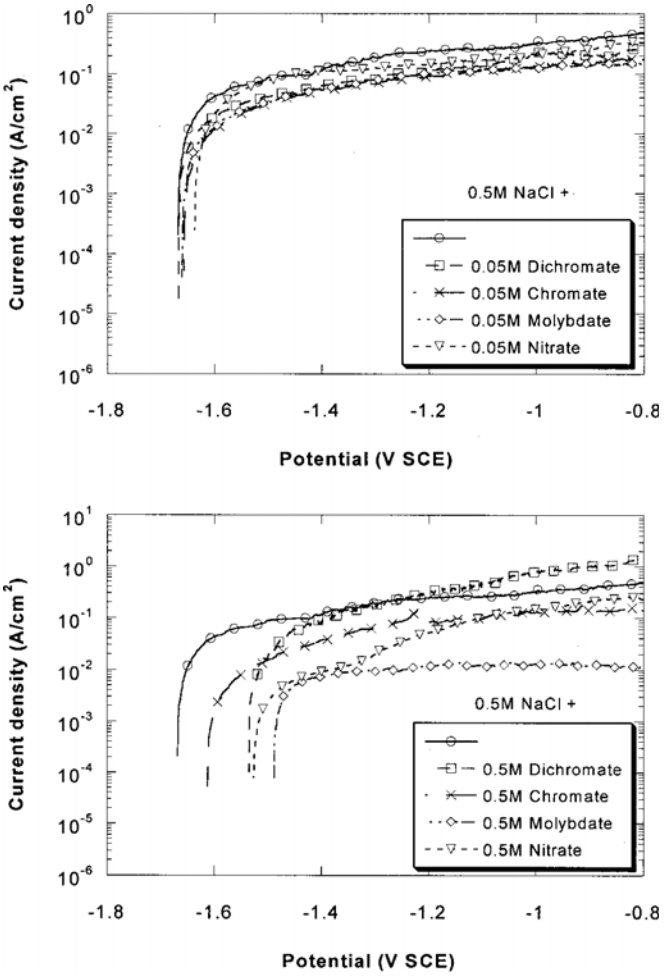

Figure 3. Effect of various inhibitor ions on Mg dissolution kinetics in 0.5 M NaCl containing (a) 0.05 M inhibitor, (b) 0.5 M inhibitor.

The same type of analysis described above to fit the potential components was applied to the Mg data, and the results are given in Table III. It should be noted that the current decayed quickly to low values in 0.5 M NaCl + 0.5M molybdate during the initial polarization, so a very long hold time was required to generate sufficient charge. The current remained low during the subsequent downward scan and application of Eq. 7 did not yield reasonable values. This behavior may have resulted from the formation of a protective film. As for the case of the Al artificial crevices, the shift in the polarization curves for the solutions containing the inhibitors results from higher values of $-b \log(i_0)$. This is particularly evident in the solutions containing 0.5 M inhibitor ions.

Table III. Values determined from Mg artificial crevice experiments.

Solution	E_{rp} (V SCE)	$\log(i_0)$ (A/cm^2)	b (V/dec)	$-b\log(i_0)$ (V/dec)	σ_{crev} (mS/cm)
0.5 M NaCl	—1.669	—25	0.041	1.025	19
0.5 M NaCl, 0.05 M dichromate	—1.668	—74	0.013	0.962	6.5
0.5 M NaCl, 0.05 M chromate	—1.658	—50	0.020	1.000	5.2
0.5 M NaCl, 0.05 M molybdate	—1.662	—24	0.047	1.128	7.0
0.5 M NaCl, 0.05 M nitrate	—1.638	—34	0.029	0.986	10
0.5 M NaCl, 0.5 M dichromate	—1.536	—87	0.012	1.185	35
0.5 M NaCl, 0.5 M chromate	—1.614	—79	0.014	1.106	5.2
0.5 M NaCl, 0.5 M molybdate	—1.489	-	-		-
0.5 M NaCl, 0.5 M nitrate	—1.527	—9.9	0.15	1.485	18

Conclusions

The influence of various inhibitor ions on the dissolution kinetics of Al and Mg in chloride-containing solution was investigated by artificial crevice electrode technique. Of dichromate, chromate, molybdate, and nitrate ions, only nitrate was found to inhibit the dissolution kinetics of the Al artificial crevice electrode. In contrast, all anions inhibited the dissolution kinetics of Mg artificial crevice electrodes. Also, this work confirms the notion that the mechanism of inhibition of Al or Al alloy localized corrosion by chromate must be something other than anodic inhibition in acidic crevices or pits.

Acknowledgments

This work was supported by the Strategic Environmental Research and Development Program under contract no. DACA72-99- C-0002, and the Air Force Office of Scientific Research under contract no. F49620-96-1-0479.

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